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MEMORANDUM FOR PRS (Contractor Publication)

17 Mar 1998

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SUBJECT: Authorization for Release of Technical Information, Control Number: **AFRL-PR-ED-TP-1998-068**
K. Christe et al. "The New Bicyclic Nitrogen Tetroxide Cation, NO_4^+ has a Low Decomposition Energy"

(Statement A)

THE NEW BICYCLIC NITROGEN TETROXIDE CATION, NO₄⁺ HAS A LOW DECOMPOSITION ENERGY.*

Anatoli A. Korkinⁱ, Rodney J. Bartlettⁱ Marcel Nooijenⁱ and Karl O. Christeⁱⁱ

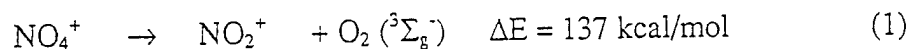
ⁱQuantum Theory Project, University of Florida, Gainesville, FL 32611-843,

ⁱⁱPhillips Laboratory, Edwards AFB, CA 93524-7680

Nitrogen oxide cations, such as NO₂⁺ and NO⁺, are strong oxidizers and useful components for ionic High Energy Density Materials (HEDM) [1]. Their energy content and oxidizing power increase with increasing oxidation state of the nitrogen atom and the number of oxygen ligands. In our search for related, halogen-free, highly energetic cations we have become interested in the bicyclic NO₄⁺ (I).

In view of the great challenge and the time consuming efforts which the synthesis of NO₄⁺ would present, and the potential for low energy decomposition pathways, it was imperative to first pursue a feasibility study using *ab initio* methods. This contribution of theory offers the synthetic chemist the benefits of avoiding the unsuccessful pursuit of target molecules which are either vibrationally unstable or possess very low barriers towards decomposition, and provides guidance for their synthetic efforts.

The gas phase heat of formation of NO₄⁺ (370 kcal/mol) has been estimated at the CCSD(T)/TZ2P level from the experimentally known heat of formation of NO₂⁺ (233 kcal/mol) and the heat of the reaction:



Although the minimum D_{2d} structure of I has short NO distances and long OO distances and is vibrationally stable at the HF, MBPT(2) and CCSD levels of theory (see Table 1), the decomposition barrier was suspected to be low because of the high exothermicity of reaction 1 (Scheme 1). The minimum energy C_{2v} path is a symmetry and spin (singlet-triplet) forbidden reaction. To model the transition barrier structure we searched for its TS and the minima at the lowest PES crossings by using the novel STEOM-CCSD method. An algorithm, which allows to locate intersystem crossing

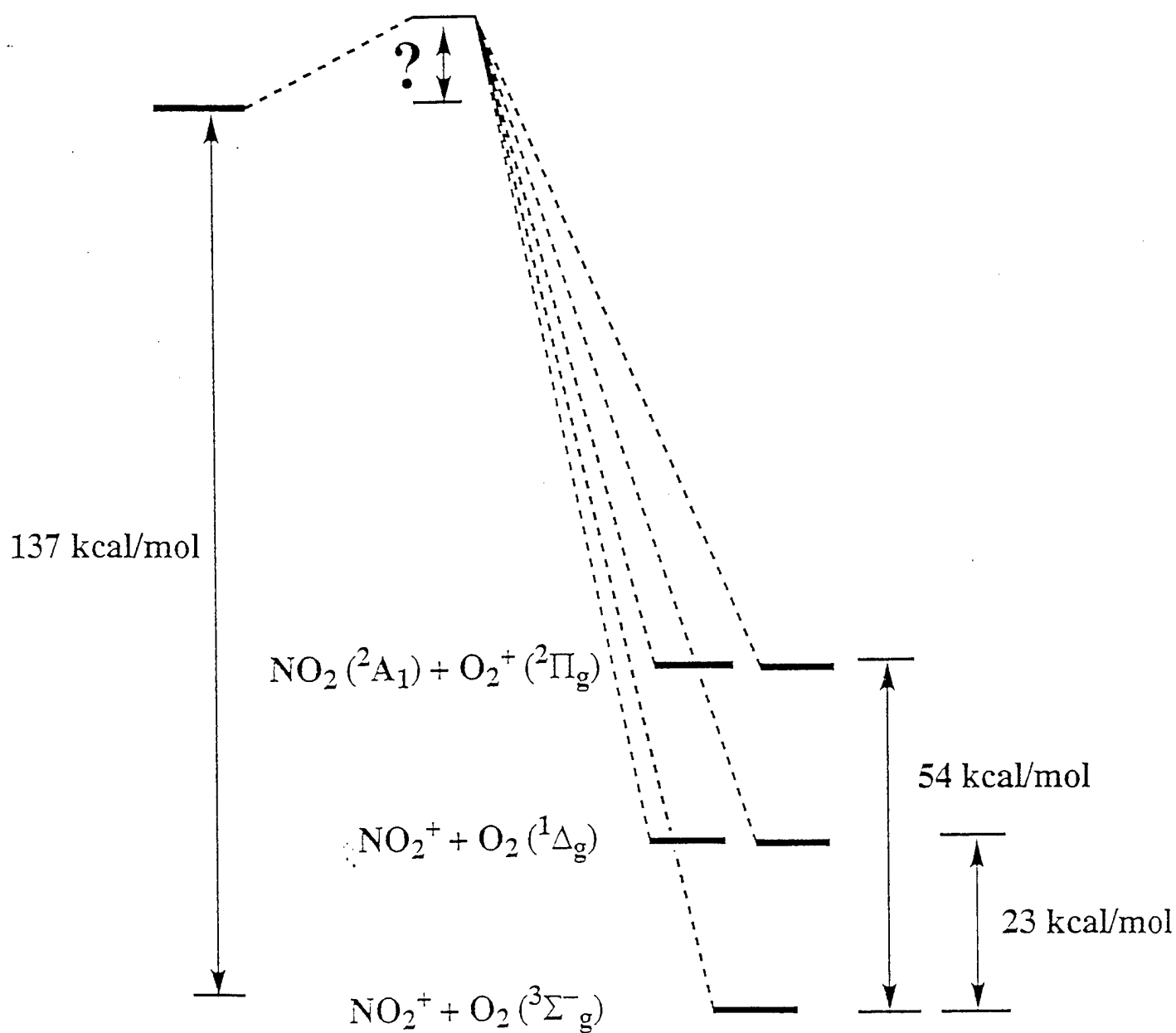
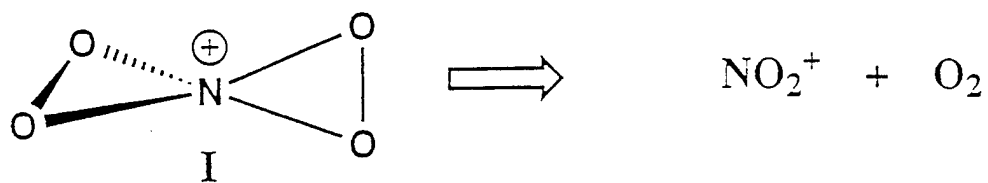
minima efficiently, has been implemented into the ACES II program recently. It is based on minimization of the functional, $F = E_1 + E_2 + \alpha * (E_1 - E_2)$, where α is an adjustable penalty parameter (usually about 10^3).

The transition state, which has been found at the 1A_1 potential energy surface, and two intersystem crossing minima, singlet-singlet and singlet-triplet, have similar structures and close energies (see Table 2). The wave function has an essential multi-configurational character in the transition state and in other computed low lying excited states (Scheme 2).

The estimated decomposition barrier has been finally computed by using CASPT2, STEOM-CCSD [2], and CCSD(T) methods with extended basis sets at the STEOM-CCSD/DZP optimized geometries. All approaches show the decomposition barrier to be too low (10-20 kcal/mol) for this cation to have any reasonable stability. In addition NO_4^+ has a high vertical electron affinity (8.4 eV compared to 4.5 eV in NH_4^+), which would be another reason for a high instability of the cation.

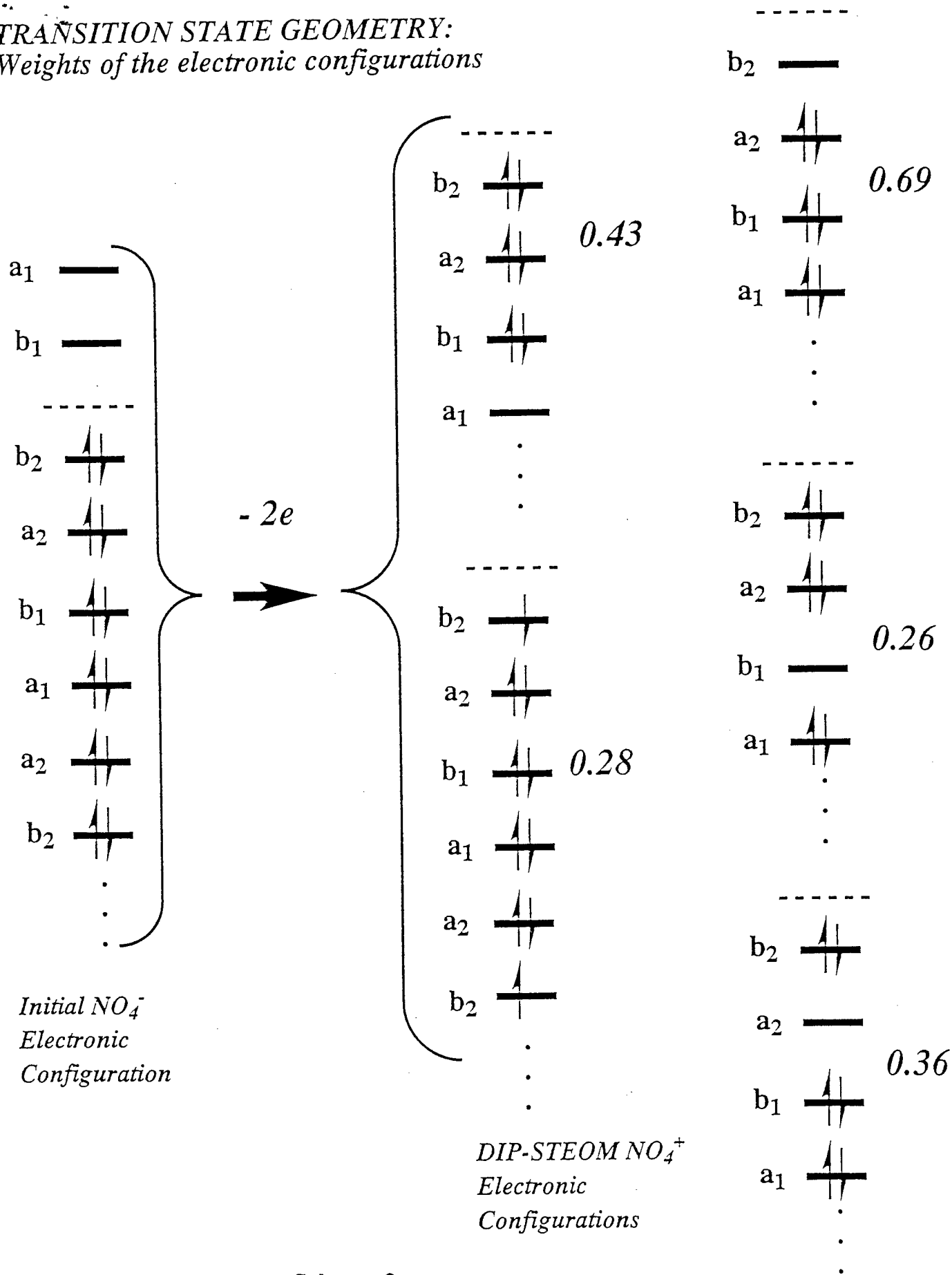
The structures of other bicyclic species, XY_4 ($X = \text{B}^+, \text{C}, \text{N}^+$; $Y = \text{N}, \text{O}$) (Scheme 3), have been computed at the MBPT(2)/6-31G* and at the CCSD/DZP levels (Scheme 3) and their energetics and reactivity are under investigation.

- [1] E.W. Lawless, I.C. Smith, Inorganic High-Energy Oxidizers (Marcel Dekker, Inc. New York, 1968).
- [2] M. Nooijen, R.J. Bartlett, J. Chem. Phys. 106 (1997) 6441.



Scheme 1

TRANSITION STATE GEOMETRY:
Weights of the electronic configurations



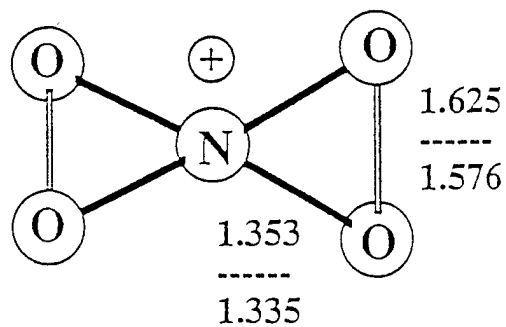
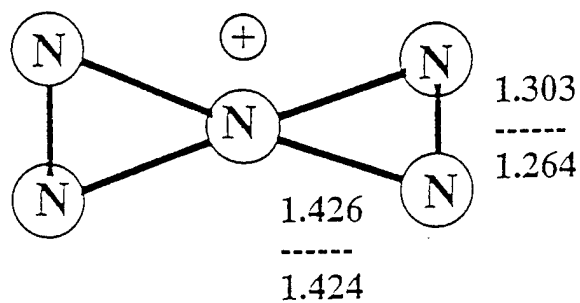
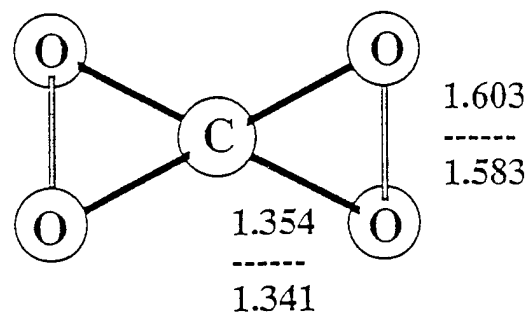
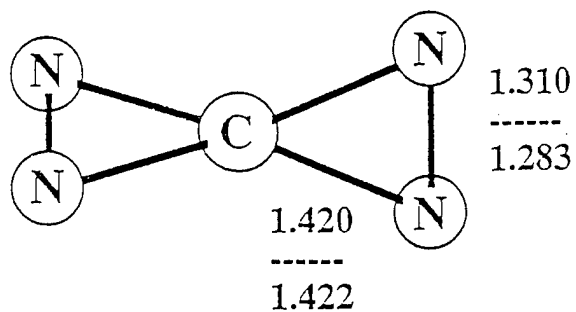
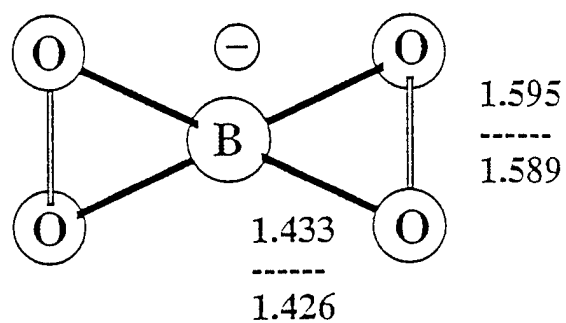
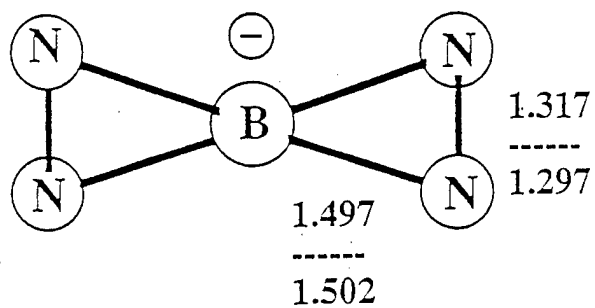
Scheme 2

XN_4

VS

 XO_4

MBPT(2)/6-31G*

CCSD/DZP

Scheme 3

Table 1.

Bond lengths (in angstroms) and harmonic vibrational frequencies (in cm^{-1}) of the $\text{D}_{2d}\text{NO}_4^{+a}$

Method:	HF/		MBPT(2)/		CCSD/	
	/DZP	/TZ2P	/DZP	/TZ2P	/DZP	/TZ2P
Bond lengths:						
R_{NO}	1.290	1.292	1.346	1.347	1.335	1.335
R_{OO}	1.455	1.467	1.620	1.613	1.576	1.571
Frequencies:						
B_1	472 (0)	466 (0)	341 (0)	340 (0)	376 (0)	377 (0)
E	556 (56)	553 (46)	511 (18)	499 (16)	505 (26)	499 (24)
A_1	696 (0)	689 (0)	563 (0)	571 (0)	554 (0)	567 (0)
B_2	942 (1)	942 (4)	664 (14)	692 (15)	679 (10)	716 (12)
E	1212 (24)	1173 (17)	967 (10)	949 (10)	1024 (16)	1005 (26)
A_1	1231 (0)	1218 (0)	913 (0)	929 (0)	981 (0)	998 (0)
B_2	1882 (100)	1832 (100)	1350 (100)	1355 (100)	1514 (100)	1502 (100)
Zero Point Energies:						
	12.52	12.29	9.70	9.70	10.24	10.25

^{a)} Relative intensities are given in parenthesis.

Table 2.

Relative energies (in kcal/mol) and structures (bond lengths in angström) of the transition state and minima at the PES crossings for a C_{2v} decomposition pathway at the STEOM-CCSD/PBS//CCSD-STEOM/DZP level.^a

MO configuration	Energy	R_{NO}^1	R_{NO}^2	R_{OO}^1	R_{OO}^2
D_{2d} NO_4^+ minimum	0.0	1.335		1.576	
Transition State	12.7	1.345	1.353	2.210	1.534
$^1A_1 - ^1B_1$ crossing	12.6	1.343	1.353	2.196	1.532
$^1A_1 - ^3B_1$ crossing	11.3	1.336	1.338	2.028	1.557

Lowest electronic state at the transition state geometry.

Multiplet	root	irrep	energy diff (eV)	% singles	total energy
Triplet	1	3B_1	14.52026902	99.98	-354.00019085
Singlet	1	1B_1	14.72766231	99.96	-353.99256929
Singlet	1	1A_1	14.73537610	99.86	-353.99228581
Singlet	1	1A_2	14.78197499	99.94	-353.99057334
Singlet	2	1A_1	14.83184913	99.87	-353.98874050

^a The D_{2d} minimum has been computed at the CCSD/DZP level.